

Study of Anatase TiO₂ in the Presence of N₂ under Shock Dynamic Loading in a Free Piston Driven Shock Tube

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Abstract

Free Piston Driven Shock Tube [FPST] is used to heat Ar and N₂ gas mixture to extremely high temperature like 9100 – 12300 K with reflected shock pressure of about 59-70 bar for about 2-4 ms duration. Shock heated nitrogen gas under this extreme temperature goes to both non-equilibrium and dissociation state. Here argon promotes heating of N₂ to higher temperature. At this extreme thermodynamic condition shock heated nitrogen gas interacts with the anatase TiO₂ at the end of the shock tube. The surface composition, electronic structure, crystal structure and surface morphology of the anatase TiO₂ sample was examined before and after shock loading using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and High-resolution transmission electron microscopy (HRTEM). The results obtained from the experimental investigations shows the formation of N doped rutile TiO_{2-x}N_x. After shock treatment colour of the top surface of white anatase TiO₂ change to yellow colour indicating nitrogen doping. Under this temperature anatase TiO₂ is subjected to super heating and cooling in presence of high enthalpy nitrogen and helps to stabilize the N doped rutile TiO₂ structure. In this short duration, crystallographic phase transformation occurs from anatase TiO₂ to N doped rutile TiO₂. An extreme thermodynamic condition prevalent at the end of the shock tube makes FPST an important tool for the exploration to study polymorphic phase transformation of ceramic materials, materials modification and synthesis of new materials.

Keywords

Shock Dynamic Loading; High-enthalpy Gas; Solar Eenergy Materials; Phase Transformation; N-Doped TiO₂

Introduction

Titania (TiO₂) is one of the most prominent materials for various kinds of industrial applications related to

energy and environmental catalysis (Hoffmann et al 1995). Three different polymorphs of TiO₂ occur in nature namely Rutile, Anatase, Brookite, beside this an additional synthetic phase called TiO₂ (B) also exist. Rutile is thermodynamically most stable phase and anatase is more kinetically favoured at lower temperature. After the discovery of photo catalytic splitting of water (Fujishima et al 1972) and solar energy conversion device (Regan et al 1991), TiO₂ considered as good photo-functional material. Enormous amount of efforts have been devoted to modification of TiO₂ to enhance its photo catalytic activity by N doping (Asahi et al 2001, Morikawa et al 2001, Irie et al 2003). N-doped titanium dioxide prepared using organic precursors and its photo catalytic activities studied under visible light (Nosaka et al 2005, Yang et al 2004). Doping of anions like carbide (C⁴⁻) and nitride (N³⁻) in anatase TiO₂ (in the form of TiO_{2-x}C_x or TiO_{2-x}N_x) were shown as alternatives to decrease the band gap of TiO₂ to achieve higher photo catalytic activity (Chen et al 2007).

In recent years, synthesis, modification of material and also phase transformation studies was performed using shock waves under extreme thermodynamic conditions. Different shock wave loading techniques are used to interact with the materials. Shock induced chemical reaction due to high strain rate for very short duration causes change in material properties (Thadhani et al 1993). Nitrogen doped titania are synthesized when the steel flyer travel with velocity ranging from 1 to 3 km/s driven by the detonation of nitro-methane which produces very high shock pressure of about 340 to 560 kbar at about 2853 K (Jianjun et al 2000, Xiang et al 2009). Here shock wave compression occurs when steel flyer impacted the

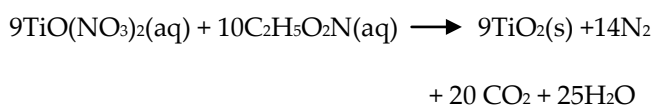
container with the samples. Laser induced shock is another method used to study semiconductor materials (Yakovyna et al 2003).

In this paper we present detailed experimental setup of free piston driven shock tube (FPST) and its application for synthesis of N doped rutile TiO_2 . A similar experimental work on phase transformation of fluorite $\text{Ce}_{0.5}\text{Cr}_{0.5}\text{O}_{2+\delta}$ on shock dynamic loading in presence of Argon gas was published elsewhere (Jayaram et al 2011). Shock tube was used to heat Ar + N_2 gas mixture to a very high temperature and at medium reflected shock pressure. At this thermodynamic condition N_2 goes to non-equilibrium state with vibrational, rotational excitation and dissociation state. We explore, the phase transformation of anatase TiO_2 to N doped rutile TiO_2 ($\text{TiO}_{2-x}\text{N}_x$) under shock dynamic loading in presence of N_2 gas using FPST.

Experimental

Synthesis of Anatase TiO_2 by Solution Combustion Method

Anatase TiO_2 was synthesized by solution combustion method (Nagaveni et al 2004). In this method, titanium isopropoxide was dissolved into water to precipitate as hydroxide. The precipitated hydroxide was dissolved in dilute HNO_3 to get 2 g of titanyl nitrate $\text{TiO}(\text{NO}_3)_2$ solution. $\text{TiO}(\text{NO}_3)_2$ solution was then mixed with 0.89 g of glycine and the resulting solution was heated in preheated muffle furnace at 623 K. Synthesized TiO_2 powder obtained after combustion was white in colour. The reaction occurs in the synthesis of anatase TiO_2 is given below.

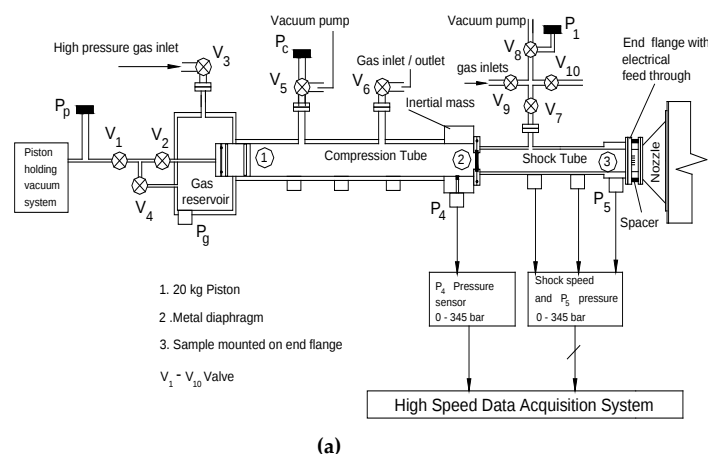


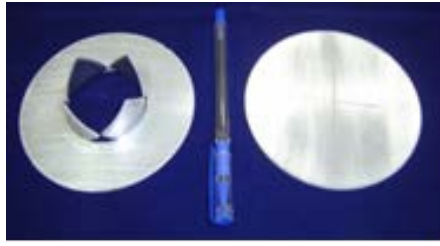
Several pellets were made to use in shock tube experiments. Each pellet was made using 100 mg of TiO_2 powder in pellet pressing machine by applying pressure up to 70 N and kept for 5 min. These pellets were used to perform shock tube experiments.

Free Piston Driven Shock Tube (FPST)

FPST established at the Institute consists of a high pressure gas reservoir, compression tube filled with 1 bar helium as driver gas and a shock tube filled with driven gas (test gas) at required pressure. Provisions

are made to mount the material on the end flange of the driven section of the shock tube. High pressure gas reservoir has the provision to mount 20 kg piston and it is held rigidly by creating vacuum behind the piston. Aluminium diaphragm is placed in between the compression tube and the shock tube. After evacuating the shock tube, gas handling system is used to fill the test gas at a required pressure. Ultra high pure (UHP) Ar is purged many times in a shock tube and then filled with equal amount of Ar and N_2 at 0.047 bar pressure as test gas. Sudden supply of the high-pressure gas by opening valves behind the piston sets its motion in the compression tube and as a result, the piston gets maximum acceleration. Motion of 20 kg piston in compression tube adiabatically compresses the helium gas and thereby increases the pressure and temperature. This high pressure and high temperature helium gas burst the Al metal diaphragms. It produces a strong primary shock wave, travelling into the driven section of a shock tube filled with test gas, which is reflected finally at the end of the shock tube to generate higher stagnation temperature and pressure. This high pressure and temperature test gas interact with the sample, mounted on the end flange of the shock tube. The block diagram of FPST along with various electronic control and data acquisition system is shown in Fig. 1a. Rupturing of aluminium diaphragm before and after the shock tube experiment is shown in Fig. 1b. The photo graph of 21 meter long FPST is shown in Fig. 2a and 2b. A simple working principle of FPST is described in earlier references (Stalker et al 1967, Kulkarni et al 2008). Design and development of the FPST, working principle and detail experimental procedure is presented elsewhere (Jayaram et al 2007, Reddy et al 2007).





(b)

FIG. 1 (A) SCHEMATIC DIAGRAM OF IISc FREE PISTON DRIVEN SHOCK TUBE (FPST) WITH ELECTRONIC CONTROLS (B) ALUMINIUM DIAPHRAGM (3MM THICK, 1/3 GROOVE) BEFORE AND AFTER RUPTURE



(a)

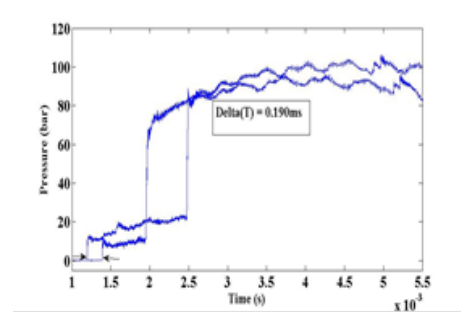
(b)

FIG. 2 PHOTOGRAPH OF COMPLETELY ASSEMBLED FREE PISTON DRIVEN SHOCK TUNNEL VIEW (A) FROM GAS RESERVOIR SIDE AND (B) FROM DUMP TANK SIDE

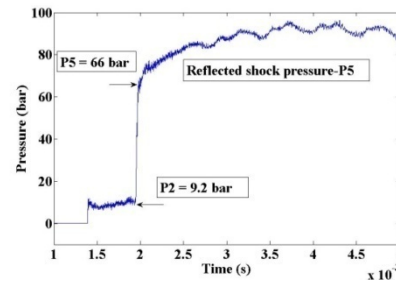
Experiments Using FPST and Estimation of Reflected Shock Temperature

Shock tube experiments was conducted by filling helium gas at 1 bar in the compression tube while shock tube were filled with equal quantities of Ar+N₂ mixture at total pressure of 0.094 bar (P₁). For the synthesis of rutile TiO_{2-x}N_x, the shock heated Ar+N₂ gas at high temperature and pressure was made to react with the anatase TiO₂ mounted at the end flange of the shock tube. The pressure behind the primary shock (P₂) and the reflected shock pressure (P₅) at the end of the driven section was measured using the commercially available piezoelectric pressure transducer (Model 113A22, PCB-Piezotronics Ltd., USA) mounted flush with the inner wall of the shock tube at the end of driven section. Multichannel high speed data acquisition system (NI PXI-6115 DAS, National Instruments Pvt. Ltd.) was used to acquire

the shock speed and reflected shock pressure data within a short test time of 2-5 ms duration. Time taken for shock to travel at a distance of 0.5 m is experimentally recorded using two pressure sensors (about 0.19 ms) and reflected shock pressure of about 66 bar at the end of the shock tube were shown in the Fig. 3a and 3b. This data are used to calculate shock velocity, shock Mach number $M_s = V_s/a_1$, where $V_s = \Delta L/\Delta t$. Where, ΔL the distance between the two pressure transducers, Δt is the time interval to travel between two sensors, a_1 is the speed of sound in driven section of the shock tube ahead of the primary shock and V_s is the measured shock speed. Pressure jump (P_2/P_1) and (P_5/P_1) also temperature jumps (T_5/T_1) for a given shock Mach number can be estimated using the following normal shock relation (Gaydon et al 1963)



(a)



(b)

FIG. 3 DATA ACQUIRED FROM PRESSURE TRANSDUCERS AT THE END OF SHOCK TUBE (A) TIME HISTORY DATA WHEN THE SHOCK TRAVELS 0.5M DISTANCE (B) REFLECTED SHOCK PRESSURE (P₅) ACQUIRED AT THE END OF SHOCK TUBE

$$\frac{P_2}{P_1} = \frac{2\gamma(M_s)^2 - (\gamma - 1)}{\gamma + 1}$$

$$\frac{P_5}{P_1} = \frac{2\gamma M_s^2 - (\gamma - 1)}{(\gamma + 1)} \left[\frac{(3\gamma - 1)M_s^2 - 2(\gamma - 1)}{(\gamma - 1)M_s^2 + 2} \right]$$

$$\frac{T_5}{T_1} = \frac{\{2(\gamma - 1)M_s^2 + (3 - \gamma)\} \{(3\gamma - 1)M_s^2 - 2(\gamma - 1)\}}{(\gamma + 1)^2 M_s^2}$$

The estimated temperature (T_5) of the test gas behind the reflected shock in the driven section of the shock tube is given as a function of shock Mach number, Specific gas constant γ (C_p/C_v) and the initial temperature T_1 of the test gas which was usually given by the ambient temperature. An experiment was conducted for different gas mixture to vary the reflected shock temperature and pressure. Table. 1 shows both experimental and estimated values using normal shock relation. Experimental results presented in the subsequent section are for the experiment condition listed in table 1(reflected shock pressure 66 bar and estimated temperature of 10500 K for 3.5 ms duration).

TABLE 1 SHOCK TUBE EXPERIMENTAL DATA AND ESTIMATED VALUES OF REFLECTED SHOCK TEMPERATURE (T_5), Γ : ESTIMATED FOR MIXTURE OF GASES

Experimental Data			Estimated Values		
(Ar+N ₂) P _i (bar)	ΔT (μ s) $\Delta L=0.5$ m	P ₅ (bar)	V _s (m/s)	M _s	T ₅ (K)
Ar: 0.047 N ₂ : 0.047 $\gamma=1.48$	190	66	2630	7.9	10500
Ar: 0.06 N ₂ : 0.06 $\gamma=1.48$	200	70	2500	7.6	9400
Ar: 0.056 N ₂ : 0.056 $\gamma=1.48$	180	61	2770	8.4	12300
Ar: 0.067 N ₂ : 0.046 $\gamma=1.5$	210	59	2380	7.3	9100

Characterizations

Different experimental techniques were used to characterize the sample before and after exposure to shock heated N₂ gas. Electronic structure of the compounds were characterized by X-ray Photoelectron spectroscopy (XPS) using Al K α radiation (1486.6 eV) where C(1s) peak at 284.5 eV was taken as reference and the accuracy of reported electron binding energy (BE) is ± 0.1 eV (MultiLab 2000, Thermo Fisher Scientific). Powder X-ray diffraction (XRD) of the compound was recorded in a Phillips X'Pert diffractometer using Cu K α radiation at scan rate of

0.25° min⁻¹ with 0.01° step size in the 2 θ range between 20° to 80°. SEM (Philips SIRION) and TEM (Technai T-20) were used to study the surface morphology and electron diffraction pattern of both anatase TiO₂ and N doped rutile TiO₂ (TiO_{2-x}N_x).

Result and Discussion

XPS was used to investigate oxidation state of Ti (2p) and N(1s) in N doped TiO₂ and anatase TiO₂. B E of Ti(2p) electron in anatase was observed at 458.5 eV (Fig. 4a), which matches well with B E of Ti(2p) electron as reported in the literature (Atuchin et al 2006). Ti(2p) B E in N doped TiO₂ was observed at 458.9 eV as shown in Fig. 4b, which was matching well with Ti(2p) B.E. of N-doped rutile TiO₂ (Saha et al 1992). Thus XPS result shows slight shift at higher binding energy in Ti(2p) peak confirms that anatase TiO₂ in converted to N-doped TiO₂ due to shock interaction. Further N doping was also confirmed after analysing N(1s) peak using XPS study. N(1s) peak at 397.5 eV in Fig. 5 confirmed that N is present in the N³⁻ ion. Nitrogen doping at higher temperature can develop a broad N(1s) peak

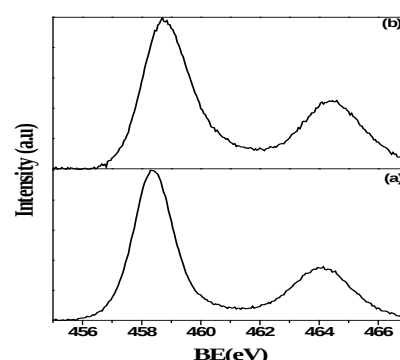


FIG. 4 (A) TI(2P) B.E. AT 458.5 eV FOR ANATASE TiO₂ AND (B) B.E. of TI(2P) AT 458.9 eV FOR N DOPED RUTILE TiO₂ FORMED AFTER INTERACTION OF SHOCK HEATED AR + N₂

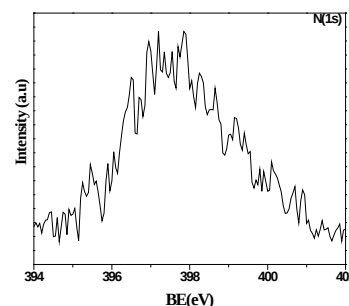


FIG. 5 XPS OF N(1S) SPECTRA IN N DOPED TiO₂ AFTER SHOCK INTERACTION

between 396 to 400 eV which was assigned to N-Ti bonding in N doped TiO₂ (Irie et al 2003, Saha et al 1992). Higher the nitrogen doped concentration, then N(1s) will have lower electron binding energy. The peak located at 397.5 eV means that N atoms are present in the TiO₂ crystal lattice in the form of Ti-N also presence in N-O bonds (Diwald et al 2004). N(1s) peak at 397.5 eV confirms the presence of O-Ti-N bond, it is accepted that nitrogen atom is located at position of oxygen sites of the N doped TiO₂ after exposure to shock in presence of N₂. The XPS data confirms nitrogen atoms have been successfully doped into the anatase TiO₂ lattice when interacted with shock heated nitrogen gas. Indexed powder XRD pattern of anatase TiO₂ (before shock) and N doped rutile TiO₂ after shock interaction is shown in Fig. 6 (a) and 6 (b). Colour of the sample before shock was white (fig. 6a inset) and aftershock

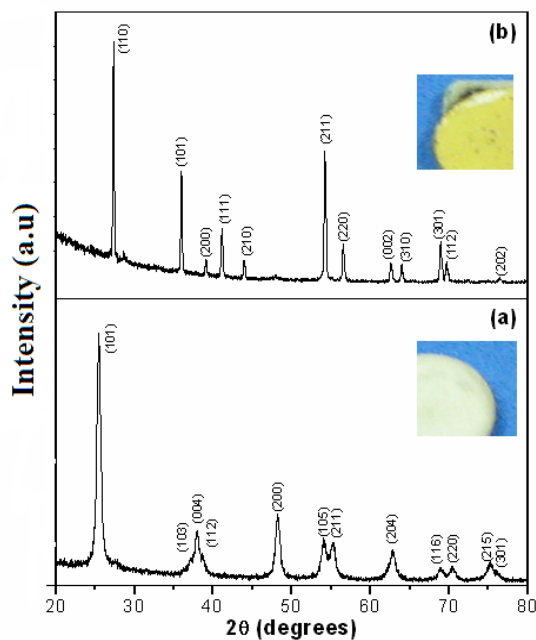


FIG. 6 POWDER XRD OF (A) WHITE ANATASE TiO₂ BEFORE SHOCK AND (B) N DOPED RUTILE TiO₂ AFTER SHOCK INTERACTION CHANGED TO YELLOW COLOUR

colour changed to yellow (fig. 6b inset) as shown in Fig. 6. XRD of shock exposed TiO₂ shows sharp peaks due to melting and re-crystallization. Structural parameters of N doped rutile TiO₂ were obtained from Rietveld refinement (Roisnel et al 2001) of Powder XRD pattern. N doped rutile TiO₂ crystallizes in tetragonal structure (JCPDS No.: 87-0920, space group: *P4₂/mmn*, lattice parameters at 300 K, *a*, *b* = 4.591(3) Å, and *c* = 2.959(2) Å). Combustion synthesized anatase TiO₂ (before shock) also exist in tetragonal structure

(JCPDS No.: 86-1157, space group = *I41/amd*, lattice parameter, *a*, *b* = 3.7913(3) and *c* = 9.527(2) Å). XRD study shows the phase transformation of anatase TiO₂ to N doped rutile TiO₂ (TiO_{2-x}N_x) due to the interaction of high enthalpy N₂ gas under shock compression.

Figure 7(a) shows SEM micrograph of cold pressed pellet of anatase TiO₂ before exposure to shock. Micrograph of N-doped rutile TiO₂ after nitridation is shown in Fig. 7b. Surface morphology of N doped TiO₂ shows surface melting and re-crystallization due to the interaction of high temperature shock heated nitrogen gas. Shock compression of anatase TiO₂ at 66 bar at high temperature (10500 K) shows unique microstructure due to dynamic re-crystallization.

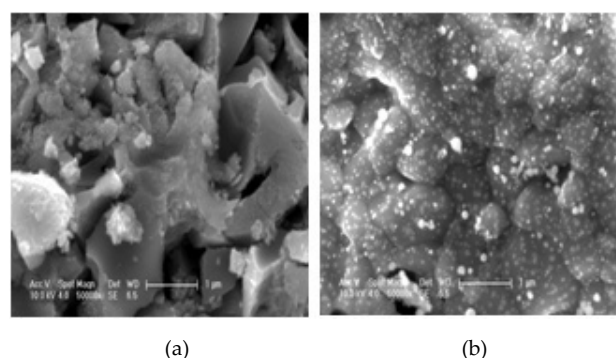


FIG. 7 SEM MICROGRAPH OF (A) ANATASE TiO₂ BEFORE SHOCK (B) N-DOPED RUTILE TiO₂ AFTER EXPOSURE TO SHOCK HEATED AR + N₂ MIXTURE

Sample for TEM were prepared by using dilute suspensions of the nanopowder before and after subjected to shock loading. These solutions were obtained by sonicating particles in acetone for 20 minutes then dropping the suspension of the sample powders onto carbon coated 300 mesh copper grid and letting it air dry for several hours. High resolution transmission electron microscope (HRTEM) studies were carried out on a sample suspended on a separate carbon grid. Bright field, HRTEM image and electron diffraction pattern indexed (101, 103, 004, 112 and 200) to anatase TiO₂ (before shock interaction) were shown in Fig. 8 (a) and 8 (b). Bright field image, electron diffraction pattern and HRTEM image (in the inset of (c)) of N doped rutile TiO₂ are shown in Fig. 8 (c) and 8 (d). Lattice fringe are at ~3.21 Å corresponding to *d*₁₁₀ rutile TiO₂ also electron diffraction indexed (110, 101, 111 and 211) to rutile structure. Absence of lattice fringes or diffraction line corresponding to anatase TiO₂ confirms that the complete phase transformation of anatase to rutile occurs due to interaction of shock heated Ar and N₂ gas mixture.

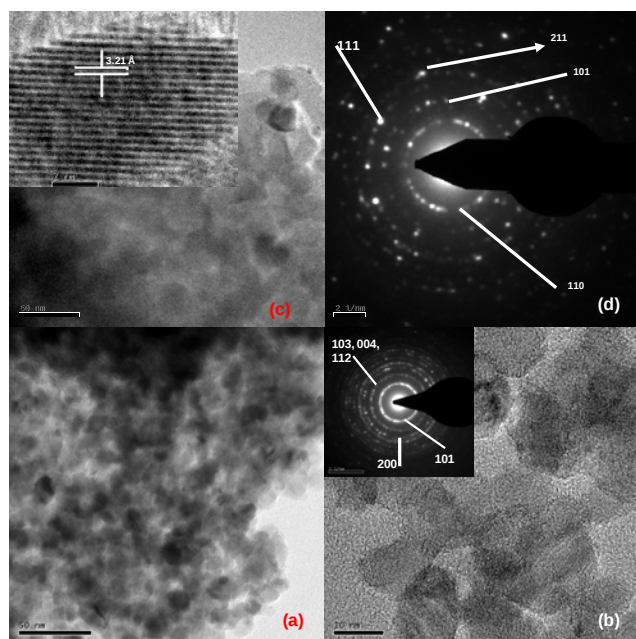


FIG. 8 (A) BRIGHT FIELD (B) HRTEM IMAGE OF ANATASE TiO₂ (BEFORE SHOCK) AND INSET OF 8(B) SHOWS INDEXED ELECTRON DIFFRACTION PATTERN (C) BRIGHT FIELD AND (D) INDEXED ELECTRON DIFFRACTION PATTERN OF N DOPED TiO₂ (RUTILE) AFTER INTERACTION OF SHOCK HEATED AR + N₂. INSET OF 8(C) SHOWS HRTEM IMAGE OF N DOPED RUTILE TiO₂.

Conclusions

In brief, we have demonstrated that the interaction of high enthalpy shock heated (Ar+N₂) gas mixture with anatase TiO₂ in shock tube transformed to N doped rutile TiO₂. Nitrogen doped Titania is achieved by various methods as reported in the literature. In the present experimental setup shock compressed nitrogen gas (66 bar pressure) at high temperature (about 10500 K) react with anatase TiO₂ for short duration (3.5 ms). This high temperature nitrogen gas reacts with anatase TiO₂, formation of N doped rutile TiO₂ is investigated using XPS, XRD, SEM and HRTEM. Both N doping and crystallographic phase transformation occurs simultaneously. Assuming that the heat transfer rates of 1/3 the total estimated temperature (10500 K) in 3.5 ms time, the super heating and cooling occurs at the rate of 10⁶ K/s. At this rate of heating and cooling, the kinetics and dynamics of phase transformation, surface reaction, material properties, and electronic structure of shock exposed materials are not well understood. In the present shock tube experiments, materials are subjected to high temperature gas impact, which is a unique method developed in our laboratory. This novel experimental technique is used to study materials under extreme thermodynamic conditions. Both theoretical and experimental investigations are

required to understand the reaction kinetics on materials due to high temperature gas impact. We hope this opens up new area of research in high temperature materials chemistry.

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